Nuclear Criticality Safety Engineering Training
Module 10 [1]

Criticality Safety in Material Processing Operations - Part 1 [2]

1.0   LESSON OBJECTIVE

This module describes the fundamental chemistry of plutonium and uranium that is applicable to the Plutonium Uranium Recovery by Extraction (PUREX) process and the Savannah River Site (SRS) H-area Modified (HM) process. General criticality safety issues are discussed, but operational controls and contingencies are deferred to Part 2 of this topic, in Nuclear Criticality Safety Engineering Training (NCSET) Module 11. A basic understanding of the chemistry is necessary to analyze the criticality safety problems that can arise during chemical separation operations.

2.0   REFERENCES

Numerous text books and references exist that cover the details of plutonium and uranium chemistry. A few of these are listed below.

1) T. L. Brown, H. E. Lemay, Jr. and B. E. Burstein, "General Chemistry, 7th Edition," Prentice Hall, New Jersey, Chapter 21.

2) In *Plutonium Chemistry*, W. T. Carnall and G. R. Choppin, Eds., "American Chemical Society Symposium Series," Kansas City, Missouri, September 12-17, 1982, American Chemical Society, Washington, D.C., 1983.

3) J. M. Cleveland, "The Chemistry of Plutonium," Gordon and Breach Science Publishers, New York, 1970.

4) H. C. Paxton and N. L. Pruvost, "Critical Dimensions of Systems Containing ^{235}U, ^{239}Pu, and ^{233}U," Los Alamos National Laboratory Report LA-10860-MS, 1986.

5) F. Weigel, J. J. Katz and G. T. Seaborg, *Chapter 7: Plutonium* in "The Chemistry of the Actinide Elements, 2nd Edition," J. J. Katz, G. T. Seaborg and L. R. Morss, Eds., Chapman and Hall, Ltd., 1986

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3.0   BACKGROUND

Nuclear reactors operate by sustaining a fission neutron chain reaction in the fuel material (typically ^{235}U). As the fuel elements "burn", several processes occur that degrade the performance of the fuel.   First, the concentration of fissile isotopes (enrichment) decreases, reducing the ability of the reactor to maintain its power level. Second, the amount of fission products increases. Since many of the fission products and their decay products capture neutrons, the efficiency of the reactor decreases. Third, blanket and target materials capture neutrons to form various products such as ^{239}Pu. ^{239}Pu is useful as fuel in fast or mixed oxide (MOX) reactors or in nuclear weapons. Some reactors have targets of ^{238}U for the specific purpose of creating ^{239}Pu.

To avoid sending the partially-spent fuel elements to a waste repository, and to retrieve valuable products such as ^{239}Pu, the fuel material may be reprocessed to separate the remaining fissile material from the fission products. The separated uranium and plutonium can be reused to fabrication new fuel elements or in weapons production. Reprocessing methods may also be used to separate ^{241}Am, a decay product that degrades the performance of ^{239}Pu, from the plutonium.   Reprocessing methods include both aqueous (e.g., solvent extraction, ion exchange, and precipitation) and pyrochemical processes (e.g., direct metal reduction, molten salt extraction, electrorefining).

At the SRS, depleted uranium targets were processed through the PUREX process in the F-Canyon facility. PUREX is a solvent extraction process that historically had separated plutonium, uranium, and fission product wastes from reactor fuel. The process was first run on a large scale at SRS in 1954, and has been adopted by Britain, France Russia and Japan. In addition, SRS processes enriched uranium fuel elements using a modified PUREX process called the HM process. The HM process partitions U, Pu and Np into three separate streams, with subsequent purification of each stream.

Both the PUREX and HM processes are compartmentalized into unit operations that include dissolution, head-end, solvent extraction, and subsequent purification operations, as shown in Figures 1 and 2, respectively. Because fissile material is being processed on a large scale, each unit operation has specific nuclear criticality safety (NCS) issues. In addition, NCS issues (e.g., the presence of fissile solids) may be transferred to downstream unit operations or new issues may emerge as a result of chemical changes or process modifications. In order to understand the criticality safety concerns that accompany separation processes, a basic understanding of the separation chemistry is necessary. Unwanted accumulations of fissile mass can be caused by such things as an imbalance in exchange columns or unexpected precipitation. This module presents an introduction to the basic chemistry of Pu and U, with some discussion of general criticality safety issues in chemical processing. The next NCSET module will consider the criticality safety issues of unit operations in more detail.
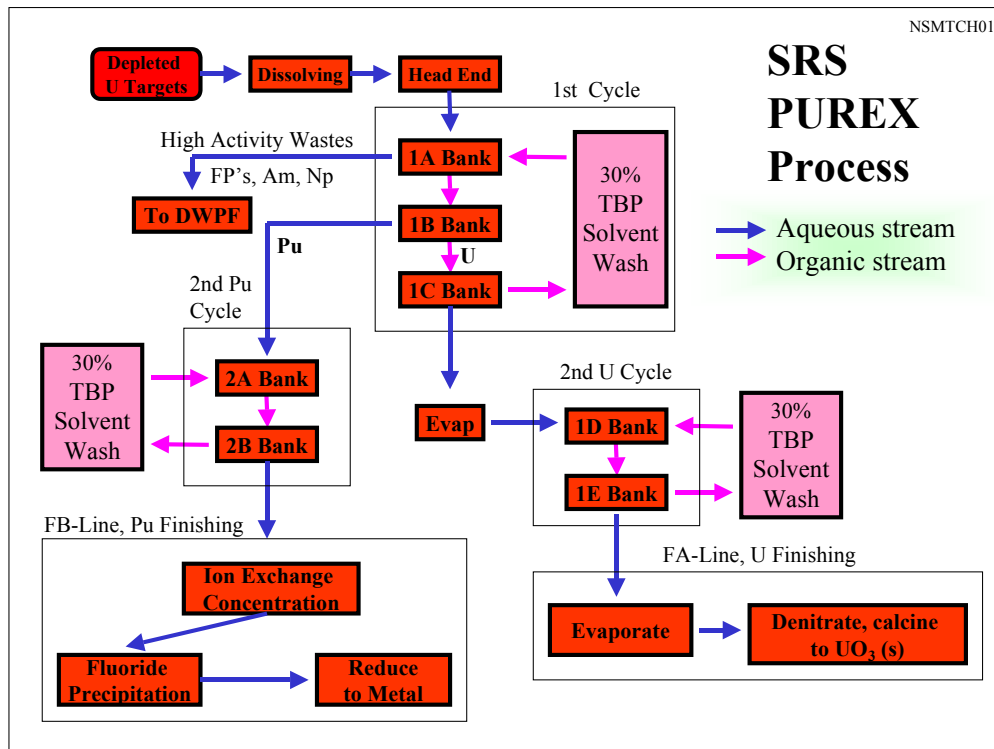
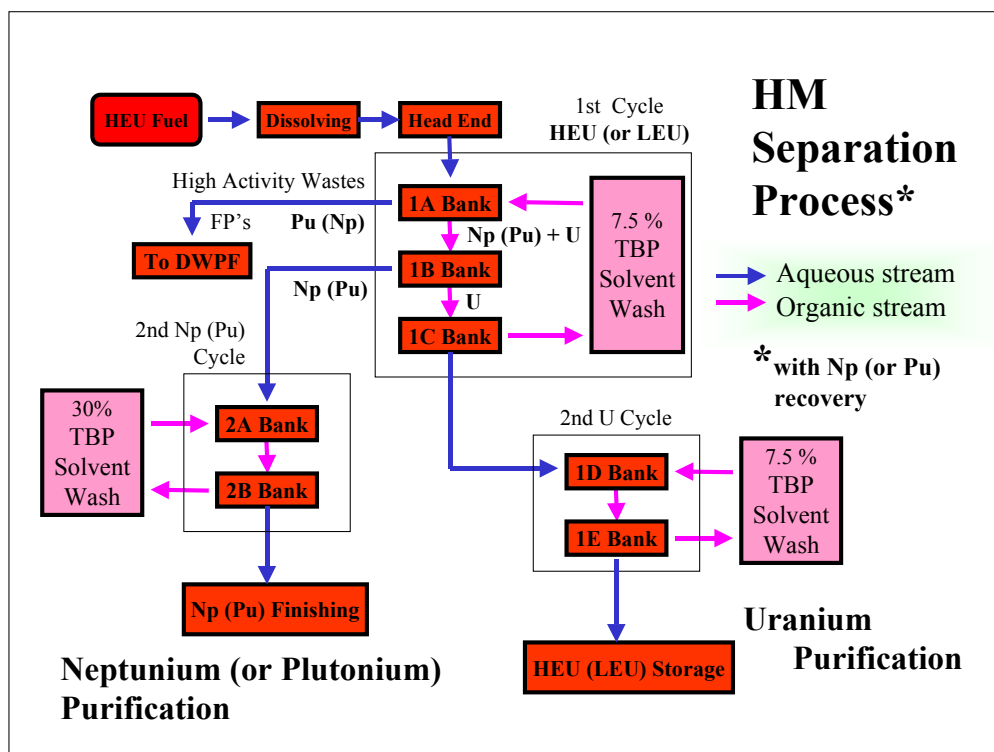Figure 1. Flowsheet for the PUREX Process

Figure 2. Flowsheet for the HM Process

4.0   FUNDAMENTALS OF PLUTONIUM AND URANIUM PROCESS CHEMISTRY

4.1   PUREX Overview

In the PUREX process, Pu (IV) and U (VI) (i.e., specific oxidation state of Pu and U, as explained below) form stable nitrate complexes that enables their separation from fission products. The Pu (IV) and U (VI) cations form neutral <u>nitrate complexes</u> that are selectively extracted into an organic phase [tri-n-butyl phosphate (TBP) extractant in paraffin diluent] whereas fission product cations generally do not form nitrate complexes, and are not extracted. After fission products have been removed, Pu and U are subsequently separated from each other based on the selective reduction of Pu to inextractable Pu (III), which is retained in the aqueous phase. U as U (VI) is not reduced and is retained in the organic phase. Subsequent purification operations are performed to polish each Pu and U product stream to attain the desired purity specifications.

4.2   Chemical Species and their Oxidation States

Since plutonium is typically produced in metallic or metal oxide forms, dissolution is required prior to aqueous processing. To oxidize the electropositive metal, mineral acids are the solvents of choice. The oxidation state (or valence) of the oxidized Pu will depend on the type of acid and other variables. The common plutonium oxidation states range from III to VI, and several oxidation states can coexist in equilibrium. The common aqueous chemical species and their oxidation states of Pu are:

Pu^{3+} is Pu (III)
Pu^{4+} is Pu (IV)
PuO_2^+ is Pu (V)
PuO_2^{2+} is Pu (VI).

In aqueous solution, uranium can exist in oxidation states from III to VI, but the VI state is the most stable and forms many complexes. The U (VI) can be reduced to U (IV) but a strong reducing agent is required. The common aqueous chemical species and their oxidation states of U are:

U^{3+} is U (III)
U^{4+} is U (IV)
UO_2^+ is U (V) [unstable]
UO_2^{2+} is U (VI) [most common].

4.2.1   Oxidation states in PUREX processing

While several oxidation states for Pu are possible, the use of acidic solutions in the PUREX process generally limits the Pu to the III, IV, or VI oxidation states. In the absence of strong reducing agents in the process, the U is exclusively in the VI oxidation state.

Changes in solution conditions (acid concentration, complexing ligand, oxidant or reductant) can alter the relative stability of different oxidation states. Under certain conditions, the aqueous plutonium may undergo self-oxidation and/or reduction (termed disproportionation). For example, in 8M nitric acid, Pu (IV) is stabilized by the oxidizing nature of the acid and the complexing by nitrate. When the solution of Pu (IV) in 8M nitric acid is diluted to lower the acidity to 0.1M, the plutonium will disproportionate to give a mixture of oxidation states III, IV and VI. This disproportionation is irreversible (i.e., not an equilibrium reaction), and may not be reversed (i.e., the Pu mixed oxidation states will not return to the IV oxidation state) by increasing the acid concentration. Under dilute acid conditions, disproportionation can <u>not</u> be avoided. To reestablish the Pu oxidation state as IV, sequential reduction to Pu (III) followed by oxidation to Pu (IV) are performed by chemical treatment.

4.2.2   Self-radiolysis

Plutonium and uranium are principally alpha-emitting radionuclides. Self-radiolysis (in addition to external gamma or X-rays) can alter the oxidation state of these radionuclides which can lead to chemical changes that could affect the processing and storage of solutions. The specific activity of each sample, which is a function of its isotopic composition and solution concentration, will determine the amount of radiation exposure it will receive from its own alpha emissions. For example, for a 0.001M (or 0.24 g/L) ^{239}Pu solution (5.15 MeV alpha particles), the rate of energy dissipation is 1.8×10^{11} eV/min. With this significant quantity of energy being released by alpha emission, the oxidation state of plutonium can be increased or decreased depending on conditions.

4.2.3   Oxidation State Control during PUREX Processing

Control of the oxidation state of plutonium is the key to the Pu-U separation in the PUREX process. Therefore, chemical adjustments to process solutions are made to manipulate separations. The chemical behavior of plutonium during PUREX processing will be determined by its oxidation state, which, in turn, defines the chemical species that is present (i.e., Pu^{3+}, Pu^{4+}, PuO_2^+, or PuO_2^{2+}). Each chemical species has unique physical and chemical properties that result in the formation of specific complexes, selective extraction into an organic phase, precipitation, volatilization, solubility, etc. Some of the chemical properties of relevant plutonium and uranium species are described below:

Pu^{3+}:   • does NOT extract into tributyl phosphate (TBP)
                • requires protection from HNO_3 to prevent oxidation to Pu (IV)
                    - sulfamic acid (HSA)is used, also called amine sulfonic acid
                • produced by treating Pu^{4+} with reducing agents:
                    - Fe^{2+} in concentrated HNO_3 (add Fe^{2+} as ferrous sulfamate)
                    - hydroxylammonium nitrate (HAN) in dilute HNO_3

Pu^{4+}:   • forms nitrate complexes:
                - extracts into TBP
                - absorbed on anion exchange resin
             • produced by:
                - Pu^{3+} and HNO_2/HNO_3 (an oxidation process)
                - PuO_2^{2+} and HNO_2/HNO_3 (a reduction process)

PuO_2^{2+}:   • forms nitrate complex
             • extracts into TBP, but not as well as Pu (IV)
             • produced by:
                - Pu^{3+}/Pu^{4+} and strong oxidizing agents (e.g. $KMnO_4$, Ce (IV))

Pu (IV) polymer (another important Pu species):
             • does not extract into TBP
             • formed in pH 1 to pH 3
             • may also form in condensate of refluxing a Pu (IV) solution in $< 6M\ HNO_3$
             • below reflux, does not form in $< 3M\ HNO_3$
             • polymer destroyed by concentrated nitric acid, heat and/or complexing agents (e.g., F^-, SO_4^{2-} etc.)

UO_2^{2+}:   • forms a neutral nitrate complex, $UO_2(NO_3)_2$
             • extracts into TBP
             • not absorbed onto anion exchange resin

4.3   Solvent Extraction Chemistry

Tri-n-butyl phosphate (TBP) dissolved in n-paraffin diluent is used to extract Pu^{4+} and/or UO_2^{2+} from an aqueous phase containing nitric acid. The solvent extraction is achieved with "extraction banks" of centrifugal contactors or mixer settlers (additional equipment details are described in NCSET Module 11). Actinide "extraction" into the organic phase is driven by a high nitric acid concentration. Therefore, the extraction process is "acid salted" rather than "Al-salted" as used in the historical Hexone Process at Hanford. The "acid salted" process creates a smaller waste volume and enables the recover and recycle of nitric acid. Below is a brief description of the chemical processes leading to this extraction.

4.3.1   Complex Formation and Extraction

Pu (IV) and U (VI) forms a neutral nitrate complexes in the aqueous phase (aq), : $Pu(NO_3)_4$ (aq) and $UO_2(NO_3)_2$ (aq). The neutral complexes form adducts (a chemical compound formed from the addition of two or more substances) with TBP at the interface between the organic and aqueous phases, and these adducts are soluble in the organic phase. When the metal species is transferred into the organic phase, we say the metal has been extracted from the aqueous phase.

4.3.2   Separation of U and Pu

To achieve separation between Pu^{4+} and UO_2^{2+}, the plutonium is selectively reduced to Pu^{3+} using a reducing agent (e.g., Fe^{2+}). When the extracted Pu species is transferred from the organic phase back into the aqueous phase, we say the metal has been <u>stripped</u> from the organic phase. In this reduction-oxidation (or "redox") process, the plutonium is reduced and the iron is oxidized, while the oxidation state of UO_2^{2+} is unaffected.

Except under unusual conditions (e.g., low acid concentration, high nitrate salt concentration), Pu^{3+} forms nitrate complexes but Pu (III) nitrate complexes are NOT extracted into the organic phase. Thus, Pu as Pu^{3+} partitions in the aqueous phase while U as UO_2^{2+} is retained in the organic phase, and thus, separation of Pu and U is achieved.

4.3.3   Uranium Stripping

Likewise, the uranium species retained in the organic phase is stripped back into the aqueous phase by reversing the extraction equilibria using dilute nitric acid solutions. The driving force for the stripping is the <u>insufficient</u> concentration of nitrate. Without relatively concentrated nitric acid solutions, the equilibrium concentration of the extractable neutral metal nitrate complex (i.e., $UO_2(NO_3)_2$ (aq)) is small. This results in the formation of water-soluble nitrate salts of UO_2^{2+} (aq).

4.3.4   Plutonium (IV) Complex Ligands

The strong affinity of plutonium (IV) for nitrate is employed in many nuclear material processing operations. Plutonium (IV) also has a strong affinity for many other complex-forming ligands (an ion, molecule or molecular group that binds to another entity to form a larger complex) such as fluoride, oxalate, peroxide, acetylacetone, carbonate and hydroxide. As a precaution, note that plutonium (IV) is prone to reaction with water (hydrolysis) around pH 3 to form an amorphous hydroxide complex, which subsequently aggregates into an insoluble hydrous polymer. At high temperatures, the polymer rapidly goes through chemical changes which makes the polymer very difficult to redissolve.

4.5   Ion Exchange Chemistry

Plutonium process streams may be purified and concentrated by cation or anion exchange.

4.5.1   Cation Exchange

The purpose of cation exchange processing of plutonium solutions is to concentrate dilute nitric acid solutions. Typically, plutonium is reduced to Pu (III) with a reductant such as hydroxylammonium nitrate (HAN) and a nitrite scavenger is employed [e.g., sulfamic acid

(HSA)] to protect the Pu (III) from reoxidation. The active sites of a typical cation exchange resin are sulfonate groups ($-SO_3H$) that exchange alkali cations (e.g., Na^+) for more electropositive cations (e.g., Pu^{3+}). In dilute nitric acid, the Pu cations are sorbed by strong ionic interactions to the sulfonate groups of the resin. Excess feed passes through the column. Desorption and elution is achieved by passing a more concentrated nitric acid solution (e.g., 5.7M HNO_3 - 0.3M HSA) through the column.

4.5.2   Anion Exchange

Anion exchange is also used to concentrate a Pu (IV) process stream, but it may also be used to separate other cationic impurities, including UO_2^{2+}. Pu (IV) forms a hexanitrato anionic complex, $Pu(NO_3)_6^{2-}$, in 7 to 8M nitric acid. To assure that the Pu is in the (IV) oxidation state, feed solutions are generally reduced with ferric sulfamate (FeSA) to give a Pu (III) solution, followed by reoxidation with sodium nitrite ($NaNO_2$) to give a Pu (IV) solution. Subsequently, the Pu (IV) solution is fed to the anion exchange column.

Reillex™ HPQ is a strong-base macroporous anion exchange resin used in the nuclear industry for its high sorption capacity for Pu (IV), radiation durability, and stability towards nitric acid. $Pu(NO_3)_6^{2-}$ sorbs to the cationic sites of the resin. Fission products, Am^{3+}, UO_2^{2+} and other metal cations that do not form anionic complexes are washed though with the feed solution. Desorption and elution is achieved by passing a dilute nitric acid (e.g., 0.35M) though the column by shifting the equilibrium away from the anionic complex.

4.5.3   Criticality Safety in Ion Exchange Operations

Because of the complexity of the ion exchange operations, multiple controls are typically used to ensure criticality safety. The following list contains typical controls.

- column dimensions chosen to be geometrically favorable
- control mass of resin (even saturated – must know sorption capacity, and compare to critical mass)
- control heel (residual Pu on column after elution) - check by mass balance, additional elution as needed
- control solids – use pre-filter to remove solids
- control feed composition – nitric acid concentration verified by refractometer measurements; dilute nitric acid (<0.01M) could lead to Pu hydrolysis and precipitation

4.6   Precipitation

In preparation for pyrochemical processing, the purified plutonium solutions need to be converted back into solids. The first step in this conversion is to treat the solution with a ligand

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that complexes plutonium and forms a precipitate. The precipitate is filtered, dried, and calcined. While various ligands have been used to precipitate plutonium, fluoride and oxalate precipitations are the most common at SRS.

4.6.1   Fluoride Precipitation

Plutonium fluoride may be prepared from Pu (III) or Pu (IV) solutions, although the best efficiency at SRS has been experienced with Pu (III). In a first stage, hydrofluoric acid solution (10%) is added to Pu (III) feed solution to induce crystal growth. Seed crystals of PuF_3 overflow into a second stage filter vessel containing 2% HF where the bulk precipitation occurs.

The PuF_3 solid is filtered, dried, and oxidized by calcination to give a mixture of PuF_4 and PuO_2 (called "converted cake"). Subsequently, the converted cake is mixed with calcium metal in a sealed pressure chamber. The calcium reacts exothermically with PuF_4 and PuO_2 to form a molten Pu / CaF_2 / CaO mixture. The dense molten Pu metal settles to bottom of crucible and forms ingots.

4.6.2   Oxalate Precipitation

Plutonium oxalate may be also prepared from Pu (III) or Pu (IV) solutions. Currently, oxalate precipitations at SRS are performed on Pu (III) solutions in slab tanks containing mechanical stirrers.

4.6.3   Criticality Safety Controls during Precipitation

During precipitation, nuclear criticality safety is primarily controlled by use of a tank that is geometrically favorable with respect to a nuclear criticality (i.e., a narrow slab tank). Other defenses include mass limits for fissile material in a tank and mass balance calculations to assure plutonium oxalate slurries have been transferred out of the tank before a new change of material is added.